



The enhancement of WO₃-catalyzed photodegradation of organic substances utilizing the redox cycle of copper ions

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ABSTRACT

WO₃ is a visible-light-responsive photocatalyst and an n-type semiconductor photocatalyst, but its photocatalytic activity toward organic substances is low. We utilized several transition metal ions as redox mediators in attempts to improve the photoactivity of WO₃, and a drastic improvement was observed only when Cu²⁺ ions were utilized for WO₃-catalyzed photodegradation of organic substances. More specifically, the CO₂ generation rates for the photodegradation of formaldehyde and methanol in the presence of Cu²⁺ ions were about 1000 and 150 times as high, respectively, as the rates in the absence of Cu²⁺ ions. We confirmed that Cu²⁺ was reduced to Cu⁺ through the transfer of a photoexcited electron from WO₃ and that Cu⁺ was easily re-oxidized to Cu²⁺ by oxygen in air. This redox cycle could assist in the reduction of oxygen in the photocatalytic reaction, and the reaction was particularly efficient when Cu²⁺ was introduced to the system as a CuCl₂ solution. Photodegradation was achieved with a WO₃ photoelectrode in a two-compartment cell in which the Cu²⁺ solution was separated from wastewater containing organic substances by an ion-exchangeable membrane, simulating practical use. The anodic photocurrent generated by the photodegradation of organic substances was observed at the WO₃ photoelectrode without applying any external bias.

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1. Introduction

Photocatalysis with sunlight or indoor light is a potentially beneficial technology for environmental purification. For example, TiO₂ under UV light is used for the degradation of harmful organic substances such as volatile organic compounds (VOCs). However, for more efficient utilization of sunlight and indoor light, visible-light-responsive photocatalysts are indispensable. Tungsten oxide (WO₃) is a visible-light-responsive photocatalyst and an n-type semiconductor photocatalyst for O₂ generation using sacrificial reagents [1–4], but reports on the degradation of organic substances by WO₃ are limited [5–11] because of its low photocatalytic activity toward organic substances in the absence of co-catalysts or redox mediators. The bottom of the conduction-band potential of WO₃ (+0.5 V vs. NHE) is more positive than both the conduction-band potential of TiO₂ (0 V vs. NHE) [12] and the one-electron reduction potential of oxygen ($E_{O_2/O_2^{\bullet-}} = 0.13$ V

vs. NHE). We suspect that the observed difficulty of O₂ reduction by an electron in the conduction band of WO₃ may be attributed to the low activity of the bare WO₃ photocatalyst. Effective promotion of WO₃-catalyzed photodegradation has been achieved by means of loading noble metal co-catalysts, such as platinum [13,14], and utilizing redox mediators, such as Fe³⁺/Fe²⁺ [9].

In a previous study, we reported the enhancement of photocatalytic activity of WO₃ by mixing it with CuO or CuBi₂O₄ powder as a co-catalyst [10,11]. These copper compounds might assist in the O₂ reduction process, but the reaction mechanism for O₂ reduction over these Cu-based co-catalysts is not clear. Moreover, in an aqueous medium, such as that encountered practically in wastewater treatment, copper compounds will dissolve as Cu ions if the wastewater is acidic. Cu ions are also expected to assist the WO₃-catalyzed photodegradation of organic substances because the TiO₂-catalyzed photodegradation has been promoted by exploiting the redox activity of Cu ions in the presence of UV light [15–22].

In this study, we performed WO₃-catalyzed photodegradation of formic acid and other organic substances in the presence and

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absence of Cu^{2+} ions under visible light, and we observed the remarkable promotion of WO_3 photocatalytic activity in the presence of Cu^{2+} ions. As a control study, we also performed TiO_2 -catalyzed photodegradation in the presence of Cu^{2+} . We observed that the color of WO_3 remained unchanged both before and after photocatalytic reactions in the presence of Cu^{2+} ions, whereas red-colored material that would prevent the irradiation of light over the photocatalyst appeared in the TiO_2 -catalyzed reaction. Here, we discuss the difference in copper redox reaction processes between WO_3 and TiO_2 , as well as the availability of copper ions in the WO_3 -catalyzed photodegradation of organic substances. These results also help in elucidating the reaction mechanism for O_2 reduction over Cu-based co-catalysts.

2. Experimental

WO_3 powder and TiO_2 powder (P-25) were obtained from Wako Pure Chemical Industries and Nippon Aerosil, respectively. Formic acid, acetic acid, formaldehyde, acetaldehyde (10 vol.% in deionized water), methanol, ethanol, isopropyl alcohol, ethylene glycol and phenol were selected as water-soluble organic substances for photodegradation studies. Aqueous solutions (0.02 M) of various transition metal chlorides (CrCl_3 , MnCl_2 , FeCl_3 , CoCl_2 , NiCl_2 and CuCl_2) were used to determine these metal ions' ability to serve as redox mediators for improving the activity of WO_3 toward photodegradation. Solutions of 0.02 M $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 were also utilized as Cu^{2+} redox mediators. Photocatalytic degradation of organic substances was conducted in a borosilicate glass vial (4.4 ml), to which a sufficient amount of photocatalyst to completely cover the bottom of the vial and 50 μl of aqueous solution were introduced. The vial was sealed with a septum cap for sampling, and then the organic substances were introduced into the vial using a syringe. Formic acid, acetic acid, formaldehyde, acetaldehyde, methanol, ethanol, isopropyl alcohol and ethylene glycol were introduced as liquids (2 μl). In the case of phenol, a aqueous solution was prepared by mixing 40 μl of 0.5 M phenol with 10 μl of 0.1 M CuCl_2 . The bottom of the vial (area: 1.1 cm^2) was irradiated with light from a xenon lamp (PerkinElmer, CERMAX LX-300). A UV cutoff filter (HOYA, L-42, $\lambda > 400 \text{ nm}$) was used with the xenon lamp for visible-light irradiation. The concentrations of CO_2 generated in the photocatalytic degradation of the organic substances were measured by a gas chromatograph (Shimadzu, GC-14B) with a flame ionization detector equipped with a methanizer. To determine the valence of the copper ions, a colorimetric reaction was performed with a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid disodium salt (bathocuproinedisulfonic acid disodium salt) dissolved in sodium acetate buffer solution (pH 5) as the color reagent.

WO_3 and TiO_2 film electrodes were used to evaluate the metal oxides' electrochemical properties in Cu^{2+} ion solution. The porous WO_3 film electrode was prepared from a precursor solution reported by Augustynski and co-workers [23], and the TiO_2 film electrode was prepared using an enhanced metal organic decomposition (EMOD) solution by SYMETRIX. Conductive glass (F-doped SnO_2 , 10 Ω/cm^2) was spin-coated with the precursor solutions and fired at 550 $^\circ\text{C}$ for 30 min. Electrochemical measurements were conducted with a potentiostat (BAS, model 630a). All electrochemical potentials are reported vs. NHE unless otherwise noted. Two types of electrochemical cells were used in the measurements: a Pyrex glass cell and a two-compartment cell separated with a Nafion membrane. A 500 W xenon lamp (UXL-500D-0, Ushio, Japan) was used as the light source for electrochemical photodegradation experiments.

3. Results and discussion

3.1. The promotion of WO_3 -catalyzed photodegradation of organic substances by various transition metal ions

The WO_3 -catalyzed photodegradation of formic acid utilizing various transition metal chloride solutions (CrCl_3 , MnCl_2 , FeCl_3 , CoCl_2 , NiCl_2 and CuCl_2) was performed under visible-light irradiation. The photocatalytic activity was evaluated in terms of the amount of CO_2 generated from the photodegradation of formic acid. WO_3 showed low photocatalytic activity in the aqueous medium in the absence of metal ions, and only CuCl_2 and FeCl_3 solutions promoted photodegradation compared with the case in the absence of metal ions. The observed activities for CuCl_2 and FeCl_3 are shown in Fig. 1. In particular, the promotion of photodegradation in the presence of CuCl_2 was drastic, and the CO_2 generation rate with CuCl_2 was obviously higher than that observed with FeCl_3 . In the presence of FeCl_3 , the activity was promoted during the initial period of reaction, but the CO_2 generation rate decreased to almost same level as that of WO_3 in the absence of metal ions after the stoichiometric equivalent of CO_2 (0.5 μmol) was generated by reduction of all of the available Fe^{3+} (1 μmol). This result may be explained as follows: During the initial period of reaction, Fe^{3+} ions were reduced to Fe^{2+} ions by consuming the photoexcited electrons in WO_3 , rather than by the oxygen reduction reaction. In photocatalytic degradation, the separation of photoexcited electrons and holes is important: It is assumed that the photoexcited holes react with organic substances, and that the photoexcited electrons reduce oxygen in the case of gas-phase reactions. However, because the dissolved O_2 concentration is low, the oxygen reduction reaction does not readily proceed in the liquid phase. This low concentration of O_2 is considered to be one of the reasons for the low observed activity of photocatalysts in the liquid phase. Therefore, we believe that the consumption of photoexcited electrons by Fe^{3+} promoted the photodegradation of formic acid during the initial reaction period. However, the rate of Fe^{2+} oxidation by oxygen in air was very slow compared with the rate of Fe^{3+} reduction by photoexcited electrons from WO_3 . Therefore, the rate of CO_2 generation decreased concurrently with the decrease in Fe^{3+} ions. WO_3 -catalyzed photodegradation experiments utilizing $\text{Ag}(\text{NO}_3)_2$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{Fe}_2(\text{SO}_4)_3$ and NaIO_3 , which are well-known electron acceptors [2–4], were also performed, and these ions also promoted the photodegradation during the initial reaction period.

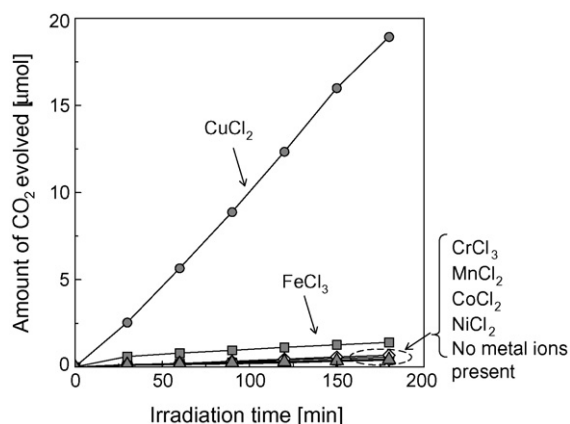


Fig. 1. The promotion of WO_3 -catalyzed photodegradation of formic acid by the metal ions tested under visible-light irradiation ($\lambda > 400 \text{ nm}$). 150 mg of WO_3 powder was used as photocatalyst in each experiment. 50 μl of aqueous solutions (0.02 M) containing various transition metal chlorides and 50 μl of deionized water were used as reaction solutions.

We believe that these reactions proceeded stoichiometrically, not catalytically. By contrast, the activity was drastically promoted in the presence of CuCl_2 , and the CO_2 generation rate remained constant throughout the duration of the reaction period. The apparent quantum yield (at $\lambda = 400 \text{ nm}$) was calculated as ca. 26% and it was also confirmed that formic acid was completely decomposed into CO_2 in this system. The WO_3 with Cu^{2+} ions showed less change in color after the reaction, whereas WO_3 without Cu^{2+} ions changed from yellow to green [24]. These results suggest that the color change of WO_3 without Cu^{2+} ions was caused by the reduction of WO_3 itself with the accumulation of photoexcited electrons. The photoexcited electrons in WO_3 were preferentially consumed by the reduction of Cu^{2+} ions in the presence of Cu^{2+} , and the self-reduction of WO_3 by the photoexcited electrons was prevented. The total amount of CO_2 generated in 3 h was ca. $19 \mu\text{mol}$, and the amount of Cu^{2+} ions initially added to the solution was $1 \mu\text{mol}$. Therefore, the turnover number of Cu^{2+} was calculated as 38 for the one-electron reduction of Cu^{2+} to Cu^+ . (A detailed discussion of the valence change of the Cu^{2+} ions is presented in the next section.) When the photodegradation of formic acid using WO_3 with Cu^{2+} ions was performed under N_2 , the CO_2 generation rate decreased after ca. $1 \mu\text{mol}$ of CO_2 was generated in the reaction, as observed for the case of FeCl_3 in air, because Cu^{2+} ions could not be regenerated by air oxidation under the inert atmosphere. These results suggest that O_2 in the gas phase was consumed during the photodegradation and that Cu^{2+} ions might be suitable as redox mediators for the catalytic reduction of O_2 . The WO_3 -catalyzed photodegradation of formic acid with CuCl_2 was repeated with varying concentration and volumes of CuCl_2 solution to optimize the reaction conditions. The maximum CO_2 generation rate was observed with 0.1 M of CuCl_2 solution, but the rate did not vary substantially from 0.02 to 0.2 M. As the volume of CuCl_2 solution was increased from 52 to $416 \mu\text{L}$, the CO_2 generation rate decreased. Furthermore, the rate under oxygen atmosphere was higher than that under air atmosphere. These results suggest that the diffusion of O_2 through the liquid phase affected the reaction rate. Therefore, sufficient aeration is necessary for the practical use of this Cu^{2+} – WO_3 system for the purification of wastewater.

The WO_3 -catalyzed photodegradation of the organic substances listed in the Section 2 was evaluated in the presence of Cu^{2+} ions. The activities for the degradation of each organic compound in the absence and presence of Cu^{2+} ions are listed in Table 1. The amount of CO_2 generated from photodegradation increased in the presence of Cu^{2+} ions for almost all the organic substances except acetaldehyde. Most notably, the CO_2 generation rates for the photodegradation of formaldehyde and methanol in the presence

of Cu^{2+} ions were ca. 1000 and 150 times as high, respectively, as those in the absence of Cu^{2+} ions.

We have previously studied the degradation of acetaldehyde in the gas phase over a WO_3 photocatalyst loaded with CuO [10] or CuBi_2O_4 [11] as co-catalysts. In those studies, we found that the CO_2 generation rate during the initial reaction period for WO_3 without co-catalyst is higher than the rates observed with CuO or CuBi_2O_4 , but that the CO_2 generation rate for WO_3 without co-catalyst suddenly levels off halfway to complete oxidation because of the formation of persistent intermediates such as formic acid, formaldehyde and acetic acid. However, complete oxidation occurs over CuO/WO_3 and $\text{CuBi}_2\text{O}_4/\text{WO}_3$; therefore, the CO_2 generation rate during the latter half of the photoreaction over WO_3 without co-catalyst is much lower than the rates observed with CuO or CuBi_2O_4 . The amount of CO_2 generation in Table 1 was compared during the initial reaction period, and the amount of liquid acetaldehyde originally added to the reaction in this study was much larger than that of gaseous one in the previous study. Furthermore, we confirmed that acetaldehyde was preferentially oxidized to acetic acid in the presence of Cu^{2+} compared with the absence of Cu^{2+} in this study. This oxidation reaction generates no CO_2 ; therefore, the amount of CO_2 generated in initial reaction period for WO_3 with Cu^{2+} was smaller than that for WO_3 without Cu^{2+} . The activities of degradation of formic acid, formaldehyde and acetic acid for WO_3 with Cu^{2+} ions were much higher than those for WO_3 without Cu^{2+} . Therefore, we surmise that the CO_2 generation rate after an extended photoreaction over WO_3 with Cu^{2+} might become higher than the rate observed without Cu^{2+} .

3.2. The difference between WO_3 - and TiO_2 -catalyzed photodegradation of formic acid in the presence of Cu^{2+}

The promotion of TiO_2 -catalyzed photodegradation of organic substances in the presence of Cu^{2+} ions under UV light has been reported previously [15–22]. Here, we compared the photodegradation activity and the reaction process of WO_3 with those of TiO_2 in CuCl_2 solution (Fig. 2). TiO_2 demonstrated photodegradation activity even without Cu^{2+} ions, whereas WO_3 showed little activity in the absence of Cu^{2+} . This difference might be explained by the negative potential of the conduction band of TiO_2 [12] compared with that of WO_3 : the potential of TiO_2 is negative

Table 1

The promotion of WO_3 -catalyzed photodegradation of various organic substances in the presence of Cu^{2+} as demonstrated by the amounts of CO_2 generated after 3 h of photodegradation

Organic substance	Amount of CO_2 generated at $t = 3 \text{ h}$ (μmol)		CO_2 (CuCl_2)/ CO_2 (no metal ions)
	No metal ions present	CuCl_2 solution	
Methanol	0.005	0.710	148.0
Ethanol	0.003	0.053	16.4
Formaldehyde	0.004	3.702	1046.1
Acetaldehyde	1.754	0.461	0.3
Formic acid	0.402	18.937	47.1
Acetic acid	0.111	1.766	15.9
Isopropyl alcohol	0.010	0.040	4.1
Ethylene glycol	0.014	1.019	75.2
Phenol	0.002	0.011	6.8

150 mg of WO_3 powder was used as photocatalyst in each experiment. $50 \mu\text{L}$ of 0.02 M CuCl_2 and $50 \mu\text{L}$ of deionized water were used as reaction solutions.

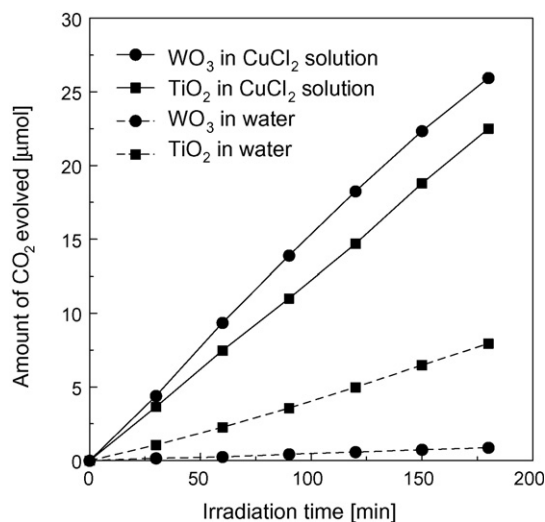


Fig. 2. The comparison of photodegradation activity for formic acid between WO_3 and TiO_2 in the presence and absence of Cu^{2+} ions under UV and visible-light irradiation. 150 mg of WO_3 powder and 15 mg of TiO_2 powder (P-25) were used as photocatalyst. $50 \mu\text{L}$ of 0.02 M CuCl_2 and $50 \mu\text{L}$ of deionized water were used as reaction solutions.

enough to reduce O_2 in photodegradation without the assistance of redox mediators. We also confirmed that the activity of TiO_2 was promoted by the presence of Cu^{2+} ions, but the promotion effect of the Cu^{2+} ions was more pronounced in the WO_3 -catalyzed photodegradation than in the TiO_2 -catalyzed reaction. The notable difference between WO_3 and TiO_2 was observed in the color of the catalysts after the reaction. (Photos of the catalysts both before and after photodegradation and after aeration are shown as [Supporting Information \[24\]](#).) The color of WO_3 with Cu^{2+} ions did not change following the photocatalytic reaction, but a red-colored material formed on the surface of TiO_2 during photodegradation with Cu^{2+} ions. This red-colored material was identified as metallic copper by X-ray diffraction measurements, in agreement with observations made by Rachimoellah and co-workers [15]. Since this red-colored material was not observed at WO_3 , the Cu^{2+} ions might have been reduced to Cu^+ instead of Cu^0 in the WO_3 -catalyzed photodegradation. The color of $CuCl$ solution is not red but approximately colorless. To determine the valence of the copper ions in the WO_3 -catalyzed photodegradation, a colorimetric reaction was performed using a bathocuproinedisulfonic acid solution as the color reagent. Bathocuproinedisulfonic acid selectively reacts with Cu^+ ions, resulting in an orange color. After photodegradation, the sample solution from WO_3 in the presence of Cu^{2+} ions showed this orange color, whereas an unreacted sample solution remained colorless. These results clearly suggest that Cu^{2+} ions were reduced to Cu^+ ions in the WO_3 -catalyzed reaction. Furthermore, the oxidation of Cu^+ to Cu^{2+} by O_2 in air has been reported [15,25], and we also observed this oxidation by comparing the UV–vis absorption spectra of the $CuCl$ solution before and after air bubbling. From an electrochemical deposition test using a conductive glass electrode, both Cu^0 and Cu^+ were observed when the applied potential was ca. 0.1 V, but only Cu^+ was observed at ca. 0.3 V. For comparison, the open-circuit potentials of the WO_3 and TiO_2 film electrodes were estimated around 0.4 and 0 V, respectively. These results suggest that Cu^0 could not be deposited electrochemically in the WO_3 -catalyzed reaction. Therefore, we suspect that the difference in the reaction process between WO_3 and TiO_2 was caused by the differences in their conduction-band potentials.

3.3. The effect of Cu salt anions on WO_3 -catalyzed photodegradation of formic acid

The promotion of WO_3 -catalyzed photodegradation of formic acid in the presence of several Cu salts (chloride, nitrate and sulfate) are compared in [Fig. 3](#). $CuSO_4$ and $Cu(NO_3)_2$ also promoted the WO_3 -catalyzed photodegradation reaction,

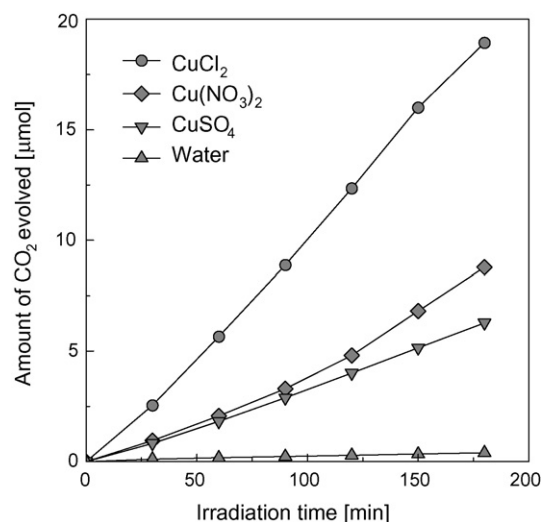


Fig. 3. The promotion of WO_3 -catalyzed photodegradation of formic acid by $CuCl_2$, $Cu(NO_3)_2$ and $CuSO_4$ under visible-light irradiation ($\lambda > 400$ nm).

whereas these solutions without WO_3 photocatalyst showed no activity. This result suggests that the Cu^{2+} ions effectively promoted the WO_3 -catalyzed photodegradation, independent of their counteranions. Chloride salt showed about twice the level of activity compared with the other Cu salts. The colorimetric reaction was performed using the Cu solutions obtained after photodegradation under N_2 to prevent the oxidation of Cu^+ , and the results are shown in [Fig. 4](#). The absorption of Cu^+ near 480 nm was observed for all of the Cu solutions after photodegradation, and the highest concentration of Cu^+ was observed for $CuCl_2$ solution. These results suggest that the Cu^{2+} ions in the $CuCl_2$ solution were more easily reduced to Cu^+ ions by photoexcited electrons over WO_3 compared with the other Cu solutions. Therefore, the high activity observed for the $CuCl_2$ solution was explained by the enhancement of charge separation due to the Cu^{2+} ions in the $CuCl_2$ solution acting as electron scavengers. Furthermore, the absorption due to the presence of Cu^+ disappeared after aeration for 2 h in all of the Cu solutions, suggesting that Cu^{2+} was regenerated by oxygen in air.

Electrochemical measurements were also performed to compare the photocurrent in these Cu salts. Current–potential properties for the three Cu salts were evaluated by the linear sweep voltammetry using platinum wire as the working and counter electrodes and a $Ag/AgCl$ (NaCl) electrode as the reference electrode. The 0.02 M, pH 4 Cu salt solutions

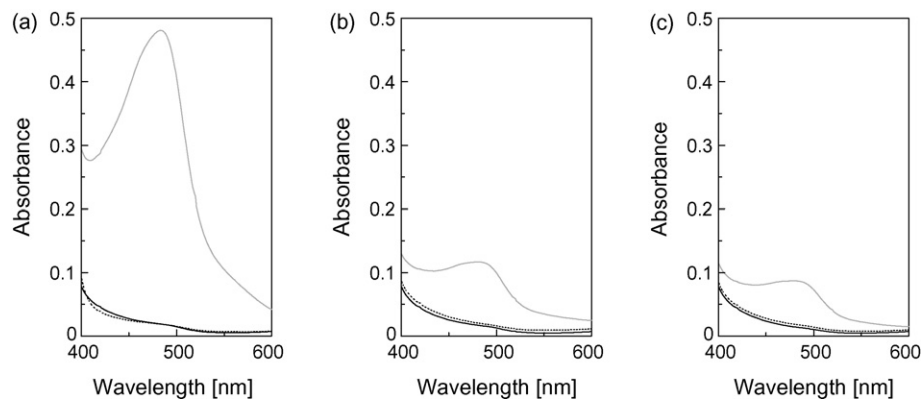


Fig. 4. UV–vis absorption spectra of (a) $CuCl_2$, (b) $Cu(NO_3)_2$ and (c) $CuSO_4$ before (black solid lines) and after (gray solid lines) reaction with bathocuproinedisulfonic acid for 2 h under N_2 . The absorbance spectra after aeration for 2 h (black dotted lines) are also shown.

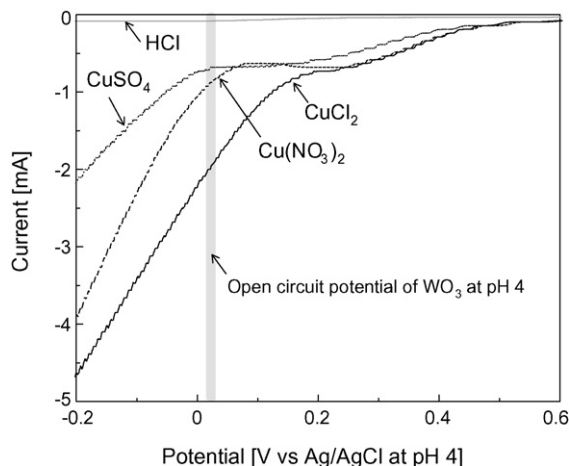


Fig. 5. The current–potential relationship observed for CuCl_2 , $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 at pH 4.

(100 ml) were used as supporting electrolytes. An HCl solution diluted at pH 4 with deionized water was used as a reference solution. The results from these electrochemical measurements are shown in Fig. 5. The cathodic currents were compared at the open-circuit potential of WO_3 (0.02 V vs. Ag/AgCl at pH 4) under UV and visible-light irradiation. This open-circuit potential is considered to be near the lower potential of the conduction band of WO_3 , and the cathodic current observed at this potential is expected to simulate the reduction ability of Cu ions in the photocatalytic reactions. All of the Cu solutions showed higher cathodic current than the HCl solution at the open-circuit potential. The highest cathodic current was observed for CuCl_2 solution, and this current was twice as high as those observed for $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 . The current density trend observed for the three Cu salt solutions follows the trend observed for their CO_2 generation rates in the photocatalytic reaction. To more realistically simulate the Cu reduction reaction in the presence of the WO_3 photocatalyst, a chronoamperometry was performed using a two-compartment cell separated with a Nafion membrane. Two WO_3 film electrodes were used for the working and counter electrodes, respectively. A 1% formic acid solution (25 ml) was used as the supporting electrolyte for the working electrode compartment, and 25 ml of Cu^{2+} solutions (0.02 M, pH 4) or HCl (pH 4) was used as the supporting electrolyte for the

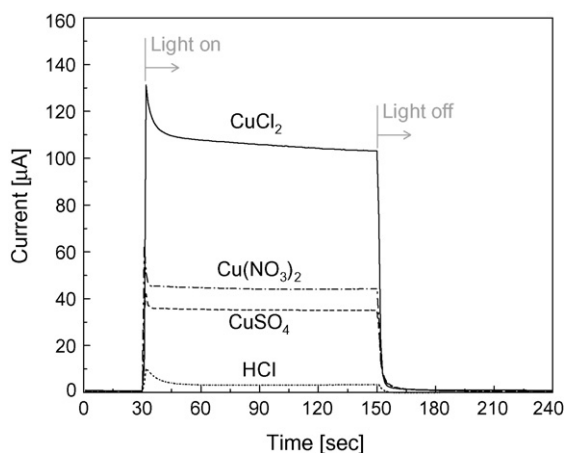


Fig. 6. The photocurrent observed at WO_3 photoelectrodes during the photodegradation of formic acid in the presence of CuCl_2 , $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 .

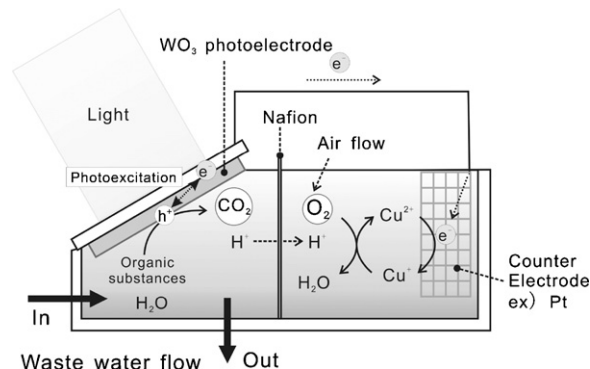


Fig. 7. A schematic of a treatment system for wastewater containing organic substances utilizing the WO_3 photoelectrode and Cu^{2+} ions.

counter electrode compartment. Only the WO_3 film electrode in the working electrode compartment was irradiated with a Xe lamp, and the photocurrent was evaluated without external bias. In Fig. 6, the photocurrents of WO_3 film electrodes were compared when the electrolyte for the counter electrode was changed. When the Cu ion solutions were used in the counter electrode compartment, the photocurrent drastically improved compared with that observed in HCl solution. The photocurrent in the CuCl_2 solution was about twice as high as the currents in the CuSO_4 and $\text{Cu}(\text{NO}_3)_2$ solutions, in agreement with the other relationships observed for photocatalytic activity. These results suggest that the reduction of Cu^{2+} ions to Cu^+ ions proceeded more easily in the presence of chloride ions than with nitrate and sulfate ions, thus promoting the high activity of WO_3 -catalyzed photodegradation in CuCl_2 solution.

In a previous study, we reported the enhancement of photocatalytic activity of WO_3 by adding CuO as a co-catalyst [9]; however, the reaction mechanism for O_2 reduction over CuO has not yet been elucidated. In the case of the CuO co-catalyst, the O_2 reduction might also be promoted by the redox mechanism of $\text{Cu}^{2+}/\text{Cu}^+$ in a manner similar to that of the Cu^{2+} ions in this study.

Finally, these two-compartment electrochemical experiments may be used as a model for practical wastewater treatment, as shown in Fig. 7. Cu^{2+} ions are inappropriate to introduce in water for environmental remediation because Cu^{2+} is also hazardous. Therefore, the Cu^{2+} ions should be separated from the flow of the treated water. By using a two-compartment cell separated with Nafion, the Cu^{2+} ions can be separated from the flow of wastewater containing organic substances. According to the results shown in Fig. 6, photodegradation using WO_3 photoelectrodes can proceed without any external bias; therefore, wastewater treatment is expected to proceed in the presence of natural sunlight by using this technique.

4. Summary

The WO_3 -catalyzed photodegradation of organic substances was highly promoted by the presence of Cu^{2+} ions, particularly those introduced to the system in a CuCl_2 solution. Cu^{2+} was reduced to Cu^+ by photoexcited electrons from WO_3 , and this Cu^+ was then easily oxidized to Cu^{2+} by oxygen in air. This redox cycle assisted in the reduction of oxygen during photodegradation. WO_3 photoelectrodes demonstrated the anodic photocurrent generated during the photodegradation of organic substances without any external bias by utilizing the Cu^{2+} solutions in a two-compartment cell separated with a Nafion membrane, so wastewater treatment under sunlight is expected to be achievable by using this technique.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2008.03.002.

References

- [1] J.R. Darwent, A. Mills, J. Chem. Soc., Faraday Trans. 2 78 (1982) 359–367.
- [2] W. Erbs, J. Desilvestro, E. Borgarello, M. Grätzel, J. Phys. Chem. 88 (1984) 4001–4006.
- [3] G.R. Bamwenda, K. Sayama, H. Arakawa, J. Photochem. Photobiol. A 122 (1999) 175–183.
- [4] K. Sayama, K. Mukasa, R. Abe, Y. Abe, H. Arakawa, J. Photochem. Photobiol. A 148 (2002) 71–77.
- [5] A. Di Paola, L. Palmisano, V. Augugliaro, Catal. Today 58 (2000) 141–149.
- [6] K.G. Kim, E.D. Jeong, P.H. Borse, S. Jeon, K. Yong, J.S. Lee, W. Li, S.H. Oh, Appl. Phys. Lett. 89 (2006) 064103.
- [7] K. Vinodgopal, I. Bedja, S. Hotchandani, P.V. Kamat, Langmuir 10 (1994) 1767–1771.
- [8] A. Sclafani, L. Palmisano, G. Marci, A.M. Venezia, Sol. Energy Mater. Sol. Cells 51 (1998) 203–219.
- [9] T. Arai, M. Yanagida, Y. Konishi, H. Sugihara, K. Sayama, Electrochemistry 76 (2008) 128–131.
- [10] T. Arai, M. Yanagida, Y. Konishi, Y. Iwasaki, H. Sugihara, K. Sayama, Cat. Commun. 9 (2008) 1254–1258.
- [11] T. Arai, M. Yanagida, Y. Konishi, Y. Iwasaki, H. Sugihara, K. Sayama, J. Phys. Chem. C 111 (2007) 7574–7577.
- [12] H.P. Maruska, A.K. Ghosh, Sol. Energy 20 (1978) 443–458.
- [13] R. Abe, B. Ohtani, Catalyst Catal. 49 (2007) 382–383.
- [14] K. Matsuoka, T. Nosaka, S. Ogawa, 77th Autumn Meeting of Chemical Society of Japan, 4P2B005, 1999 (Abstract).
- [15] M. Bideau, B. Claudel, L. Faure, M. Rachimoellah, Chem. Eng. Commun. 93 (1990) 167–179.
- [16] M. Bideau, B. Claudel, L. Faure, H. Kazouan, J. Photochem. Photobiol. A Chem. 61 (1991) 269–280.
- [17] M. Bideau, B. Claudel, L. Faure, H. Kazouan, J. Photochem. Photobiol. A Chem. 67 (1992) 337–348.
- [18] N.S. Foster, R.D. Noble, C.A. Koval, Environ. Sci. Technol. 27 (1993) 350–356.
- [19] C. Shifu, L. Yunzhang, Chemosphere 27 (2007) 1010–1017.
- [20] M. Fujihira, Y. Satoh, T. Osa, Bull. Chem. Soc. Jpn. 55 (1982) 666–671.
- [21] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, A. Itaya, Bull. Chem. Soc. Jpn. 58 (1985) 2015–2022.
- [22] M.J. López-Muñoz, J. Aguado, B. Rupérez, Res. Chem. Intermed. 33 (2007) 377–392.
- [23] C. Santato, M. Odziemkowski, M. Ulmann, J. Augustynski, J. Am. Chem. Soc. 123 (2001) 10639–10649.
- [24] The photos of the catalysts before and after photoreaction, and after aeration can be shown as electronic supplementary materials in web site.
- [25] A. Kunai, S. Hata, S. Ito, K. Sasaki, J. Org. Chem. 51 (1986) 3471–3474.